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(54) PROCESS FOR PRODUCING BUTYRALDEHYDES

(71)   We, MITSUBISHI CHEMICAL IN-
DUSTRIES LIMITED, a Japanese company, of
No. 5-2, Marunouchi 2-Chome, Chiyoda-ku,
Tokyo, Japan, do hereby declare the inven-
5 tion, for which we pray that a patent may be
granted to us, and the method by which it
is to be performed, to be particularly des-
cribed in and by the following statement:—

10   This invention relates to a process for
producing butyraldehydes which are rich in
the straight chain isomer and which com-
prises hydroformylating propylene in the
presence of rhodiumtriarylphosphine com-
15 plex catalyst.
   Recently, the hydroformylation reaction of
olefins using rhodium catalysts has been
atcively investigated since rhodium catalysts
possess a high catalytic activity and a high
20 seletcivity to aldehydes in the hydroformyl-
ation of olefins. In particular, rhodium com-
plex catalysts in which biphyllic ligands such
as tertiary phosphines are coordinated with
rhodium metal are known to be advantage-
25 ous in the hydroformylation of α-olefins, be-
cause catalysts of this type exhibit a high
selectivity to straight chain aldehydes, which
are more valuable than branched chain alde-
hydes, and a hydroformylation reaction using
30 these catalysts can be conducted under pres-
sures lower than those used in conventional
hydroformylation reactions. In addition,
because of their high stability, these catalysts
can be re-used by separating the reaction
35 product by distillation into aldehydes and a
reaction solvent containing the rhodium-
tertiary phosphine complex catalyst and re-
cycling the reaction solvent containing the
catalyst into a reactor for the hydroformyl-
40 ation reaction.
   For example, Japanese Patent Publication
No. 10729/1970 discloses a method for using
an excess of organophosphorus compound in
the hydroformylation of olefins in the pres-
45 ence of a soluble rhodium complex catalyst
in which a tertiary organophosphorus com-
pound is coordinated with rhodium metal.
This reference teaches that the use of an
excess of the organophosphorus compound
50 serves to keep the catalytic activity high and

to improve the selectivity to straight chain
aldehydes.
   Also, U.S. Patent Specification No.
3,527,809 discloses a method for the hydro-
formylation of α-olefins under low pressures 55
in the presence of a rhodium complex cata-
lyst in which a biphyllic ligand having a
ΔHNP value of at least about 425 is co-
ordinated with rhodium metal. The dis-
closure in Example 76 of this Specification 60
is that the molar ratio of the straight chain
isomer to the branched chain isomer of the
aldehydes produced can be as high as 30:1
by hydroformylating hexene-1 under a water
gas pressure of from 90 to 120 psig in the 65
presence of a rhodium-triphenylphosphine
complex catalyst.
   Various studies have been made on the
effect of ligands in the low-pressure hydro-
formylation of olefins using rhodium as a 70
catalyst. However, the relationship between
the reaction pressure and the selectivity to
straight chain aldehydes has not yet been
investigated in detail. It is suggested in the
above-mentioned U.S. Patent Specification 75
No. 3,527,809 and in J. Chem. Soc. (A), p.
3133—3142 (1968) that the lower the water
gas pressure, the higher the selectivity to
straight chain aldehydes.
   In view of the above relationship between 80
the water gas pressure and the selectivity to
straight chain aldehydes as well as of the
properties of the rhodium complex catalyst,
i.e. the fact that the catalyst is stable even
under low water gas pressure, the hydro- 85
formylation reaction using a tertiary organo-
phosphorus rhodium complex catalyst has
conventionally generally been conducted
under a relatively low pressure. Commonly,
reactions conducted under a low pressure are 90
economical because of low plant-building
costs and low equipment-operating costs.
   However, it has now been found that the
relationship between the reaction pressure
and the selectivity to straight chain isomers 95
in the hydroformylation of propylene is not
as simple as the references cited above would
indicate. These investigations have revealed
that, in the hydroformylation of propylene
in the presence of a rhodium complex in 100

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which a triarylphosphine is coordinated with rhodium metal (hereinafter referred to as "rhodium-triarylphosphine complex"), the selectivity to straight chain aldehydes varies widely depending upon the phosphine concentration in the reaction solvent and the water gas pressure. Also, a unique phenomenon has been found in that at low phosphine concentrations the ratio of the normal form to the iso forms of butyraldehyde produced (hereinafter referred to as "n/i ratio") exhibits its maximum value under a water gas pressure in a specific range.

On the other hand, when a catalyst solution which contains a rhodium-tertiary phosphine complex separated from the reaction product is recycled for re-use, high boiling by-products and the catalyst, which has been deactivated due to reaction inhibitors contained in the feed propylene and water gas, accumulate incrementally in the catalyst solution. Thus, it becomes necessary to withdraw a portion of the catalyst solution and to replace it with fresh catalyst solution in order to keep the catalytic activity constant. In other words, the amount of rhodium and phosphine lost in the withdrawn portion of the recycled catalyst solution becomes higher as the concentration of rhodium and of tertiary phosphine increases. Accordingly, it is desirable to carry out the reaction at a low rhodium and phosphine concentration and yet to achieve a high selectivity to n-butyraldehyde.

An object of this invention is to provide a process for producing butyraldehydes which are rich in the straight chain isomer.

Another object of this invention is to provide a process for producing butyraldehydes, in which the loss of phosphine and rhodium can be minimized.

According to the present invention there is provided a process for producing butyraldehydes which comprises reacting propylene with a water gas in a reaction solvent containing a triarylphosphine and a soluble rhodium complex in which a portion of the triarylphosphine is coordinated with rhodium metal, under a carbon monoxide-hydrogen total pressure of from 30 to 100 kg/cm² and at a temperature of from 60 to 150°C, the total amount of the triarylphosphine present in the reaction solvent and coordinated with rhodium metal in the soluble rhodium complex being from 1 to 30 m moles per litre of the reaction solvent.

In accordance with the process of this invention, butyraldehydes are produced by hydroformylation of propylene in a reaction solvent having a low phosphine concentration. The process of this invention is hereinafter described in greater detail.

The catalyst used in the hydroformylation of this invention is a rhodium-triarylphosphine complex. The phosphine most pre-

ferred as a ligand is triphenylphosphine, but the aryl group may be a phenyl group bearing as a substituent an alkyl group having up to four carbon atoms (e.g. a methyl group). The catalyst can be prepared by any one of various conventional procedures, for example, a complex such as hydrocarbonyl tris(triphenylphosphine)rhodium. However, the catalyst can be prepared most easily and advantageously on an industrial scale by dissolving a readily available rhodium compound, for example, an organic or inorganic salt of rhodium such as rhodium acetate, rhodium nitrate or rhodium sulphate in an appropriate solvent, such as water, an organic acid such as acetic acid, an alcohol such as methanol, or an ester such as γ-butyrolactone, introducing the resultant solution into a reactor for the hydroformylation reaction, thereby forming a complex in situ in the presence of triarylphosphine.

Although the exact form of the rhodium-triarylphosphine complex which is active in the hydroformylation reaction is not completely clear, the catalyst is considered to function by forming a complex in which the phosphine, carbon monoxide, olefin and hydrogen are coordinated with rhodium. In this case, however, the active complex does not exist in a definite form and it appears that various complexes, each having different ligands due to competitive coordination of the various individual ligands, are present, the equilibrium varying with the concentration of each ligand.

The phosphine functions to increase the stability of the complex upon coordination with rhodium, but in order to obtain a catalyst having a sufficient stability to recycle it for re-use, it is desirable that more than about 5 moles, generally from 5 to 200 moles of a phosphine is present per gram-atom of rhodium. Generally, the value of the n/i ratio tends to increase as the phosphine concentration increases and, therefore, it is advantageous to use a high concentration of the phosphine from the standpoint of a high selectivity to n-butyraldehyde. However, the use of a high phosphine concentration is not economical in view of the loss of the phosphine since a portion of the recycled catalyst solution should be continuously withdrawn and replaced by a fresh catalyst solution during the reaction in order to prevent the accumulation of an inactivated catalyst and high boiling by-products. In addition, it is very difficult to dispose of waste catalyst solution containing a large amount of phosphine and to recover only the phosphine from the waste catalyst solution which also contains various high boiling by-products. For the above reasons, it is highly desirable to increase the selectivity to n-butyraldehyde at a phosphine concentration as low as pos-

sible in practising the hydroformylation reaction on an industrial scale.

According to the investigations on the hydroformylation reaction of propylene using the above rhodium-triarylphosphine complex as a catalyst, the n/i ratio of the butyraldehydes produced varies, as described below, depending upon the water gas pressure and the phosphine concentration. In the following description, the phosphine and rhodium concentrations are given at 20°C and atmospheric pressure.

At a phosphine concentration below about 30 m moles per litre of the reaction solvent, the n/i ratio reaches its maximum when the hydroformylation reaction is carried out under a total pressure of carbon monoxide and hydrogen (hereinafter referred to as "water gas partial pressure") in the range of from about 30 to 100 kg/cm², with the n/i ratio decreasing at a water gas partial pressure lower than about 30 kg/cm² or higher than about 100 kg/cm². At a phosphine concentration in the range of from about 30 to 50 m moles per litre of the reaction solvent, the n/i ratio is substantially constant under a water gas partial pressure below about 100 kg/cm² regardless of the pressure. At a phosphine concentration higher than about 50 m moles per litre of the reaction solvent, the n/i ratio tends to increase as the water gas partial pressure decreases which is consistent with observations in the cited references.

Reference is now made to the accompanying drawing which is a graph showing the relationship between the water gas partial pressure and the n/i ratio of the butyraldehydes produced in the hydroformylation reaction, using a rhodium concentration of 10 mg (calculated as rhodium metal) per litre of toluene as a reaction solvent, at a reaction temperature of 120°C at various concentrations of triphenylphosphine. Curves 1, 2, 3 and 4 show the results obtained in hydroformylation at triphenylphosphine concentrations of 100 m moles, 30 m moles, 10 m moles and 1 m mole, respectively, per litre of toluene.

Thus, in the process of this invention, the hydroformylation is advantageously carried out at a phosphine concentration below about 30 m moles but higher than about 1 m mole per litre of the reaction solvent in order to assure stability of the complex catalyst sufficient to permit the circulation of the catalyst, and at a water gas partial pressure of from about 30 to 100 kg/cm².

In the process of this invention, the rhodium concentration in the catalyst solution affects the reaction rate but is not a factor which is capable of varying the n/i ratio of the product. Accordingly, the rhodium concentration can be determined by considering both the improvement in the re-

action rate obtainable by increasing the rhodium concentration and the increase in the cost of the catalyst associated therewith. Generally, the rhodium concentration is from about 0.1 to 500 mg, preferably from 5 to 100 mg, per litre of the reaction solvent calculated as rhodium metal.

Generally, the reaction proceeds more rapidly as the reaction temperature increases, as is commonly observed in general in chemical reactions. However, the n/i ratio rather decreases at high temperatures, thereby resulting in a decrease in the yield of the desired butyraldehydes. A preferred reaction temperature is from 60 to 150°C.

Suitable solvents which may be used in the hydroformylation of this invention are those having a boiling point higher than that of butyraldehydes (e.g., above about 75°C at 1 atm) and which are inert, since these solvents make it possible to re-use the reaction solvent and the catalyst contained therein by continuously recycling the catalyst and reaction solvent to the reaction system after the butyraldehyde product has been separated by distillation from the reaction product. Examples of solvents are aromatic hydrocarbons such as toluene and xylene; saturated aliphatic hydrocarbons such as decane, tetradecane and octadecane; alcohols such as butanol and 2-ethylhexanol; and esters such as butyl acetate and γ-butyrolactone. If desired, butyraldehydes which are reaction products may be used as a reaction solvent.

The molar ratio of hydrogen and carbon monoxide in water gas used in the present invention is not critical, but generally a water gas comprising from $1/_3$ to 7 moles of hydrogen per mole of carbon monoxide can advantageously be used in the present invention.

As described above in detail, the hydroformylation reaction of propylene according to the process of this invention minimizes the loss of rhodium and phosphine and, in addition, makes it possible to produce butyraldehydes having a high proportion of n-butyr aldehyde. The process is thus extremely useful on an industrial scale.

The present invention will now be illustrated by the following Examples in which, unless otherwise indicated, all percentages, parts, ratios and the like are by weight.

GENERAL EXPERIMENTAL PROCEDURE USED IN THE EXAMPLES AND REFERENCE EXAMPLES

A 200 ml autoclave equipped with a magnetic stirrer was charged with 50 ml of toluene and a predetermined amount of triphenylphosphine and rhodium acetate. The autoclave was then purged with argon gas and 250 m moles of propylene were fed into the autoclave. The autoclave was then adjusted to the predetermined temperature and

the reaction was initiated by introducing a mixed gas of carbon monoxide and hydrogen (molar ratio of $H_2/CO=1.17$) to a predetermined pressure. In order to supplement the consumption of the gas due to the reaction, a mixed gas having the same molar ratio was supplied during the reaction to the autoclave from a gas bomb connected to the autoclave through a means for maintaining the gas pressure of the autoclave constant. When the consumption of the gas ceased, which was considered to indicate the completion of the reaction, the autoclave was allowed to cool, and the gaseous phase and the liquid phase were subjected to gas chromatography to determine the amount of propylene which remained unreacted and the amounted of butyraldehydes produced. The results obtained in each instance showed that the conversion of propylene was more than 99% and the selectivity to butyraldehydes was more than 98%.

In the following Examples and Reference Examples, the pressure is indicated in terms of a total pressure. Although the partial pressure of water gas cannot be defined independently since the partial pressure varies with the reaction temperature, the propylene concentration and the conversion of propylene, the relationship between the total pressure and the water gas partial pressure under the reaction conditions used in the Examples and Reference Examples is shown in Table 1 below.

TABLE 1

Reaction Temperature (°C)	Total Pressure (kg/cm²G)	Partial Pressure of Water Gas (kg/cm²)	
		At Initiation of Reaction	At Termination of Reaction
120	20	4	19
120	50	34	49
120	75	59	74
120	100	84	99
120	120	104	119
120	160	144	159
120	200	184	199
90	20	8	20
90	50	38	50
90	75	63	75

Solvent: Toluene
Initial Concentration of Propylene: 5 moles/litre of toluene

EXAMPLES 1 to 7

These Examples were carried out in accordance with the procedure as set forth previously but using rhodium at a concentration of 10 mg per litre of toluene calculated as rhodium metal. The reaction conditions used in these Examples and the n/i ratio of the resulting butyraldehydes are shown in Table 2 below.

TABLE 2

Reference Example No.	Total Pressure (kg/cm²G)	Reaction Temperature (°C)	Concentration of Triphenylphosphine (m mole/litre toluene)	n/i Ratio
1	50	120	10	1.79
2	75	120	1	1.66
3	75	120	10	1.80
4	75	120	30	1.83
5	100	120	10	1.78
6	50	120	1	1.50
7	50	90	10	2.04

Comparable results to those shown in Table 2 above were also obtained when the
above reaction was carried out in a continuous manner or when the above reaction
was carried out using repeatedly a catalyst-containing toluene solution obtained by sep-
arating the resulting butyraldehydes from the reaction mixture by distillation

REFERENCE EXAMPLES 1 to 10

These Reference Examples were carried out in accordance with the procedure as set
forth previously but using rhodium in a concentration of 10 mg per litre of toluene,
triphenylphosphine at a concentration of 1 to 30 m moles per litre of toluene and a total
pressure less than 30 kg/cm²G. The results obtained are shown in Table 3 below.

TABLE 3

Reference Example No.	Total Pressure (kg/cm²G)	Reaction Temperature (°C)	Concentration of Triphenylphosphine (m mole/litre toluene)	n/i Ratio
1	20	120	1	1.16
2	20	120	10	1.47
3	20	120	20	1.64
4	20	120	30	1.79
5	120	120	1	1.53
6	120	120	10	1.73
7	120	120	30	1.81
8	160	120	1	1.47
9	200	120	1	1.38
10	20	90	10	1.91

REFERENCE EXAMPLES 11 to 14

These Reference Examples were carried out in accordance with the procedure as set
forth previously but using rhodium at a concentration of 10 mg per litre of toluene,
triphenylphosphine at a concentration of at least 50 m moles per litre of toluene. The
reaction conditions used in these Reference Examples and the results obtained are shown
in Table 4 below.

TABLE 4

Reference Example No.	Total Pressure (kg/cm²G)	Reaction Temperature (°C)	Concentration of Triphenylphosphine (m mole/litre toluene)	n/i Ratio
11	20	120	100	2.22
12	20	120	50	1.94
13	50	120	100	1.96
14	75	120	100	1.95

REFERENCE EXAMPLES 15 to 18

These Reference Examples were carried out in accordance with the procedure as set
forth previously but using rhodium at a concentration of 100 mg per litre of toluene
calculated as rhodium metal and at a reaction temperature of 90°C. The reaction con-
ditions used in these Reference Examples and the results obtained are shown in Table 5
below.

TABLE 5

Reference Example No.	Total Pressure (kg/cm²G)	Reaction Temperature (°C)	Concentration of Triphenylphosphine (m mole/litre toluene)	n/i Ratio
15	20	90	100	2.45
16	50	90	100	2.04
17	75	90	100	1.96
18	20	90	10	1.87

REFERENCE EXAMPLES 19 to 20

The Reference Examples were carried out in accordance with the procedure as described in the Examples but using triphenylphosphite in place of triphenylphosphine. The reaction conditions used in these Reference Examples and the results obtained are shown in Table 6 below.

TABLE 6

Reference Example No.	Total Pressure (kg/cm²G)	Reaction Temperature (°C)	Concentration of Triphenylphosphite (m mole/litre toluene)	n/i Ratio
19	20	120	10	1.76
20	50	120	10	1.60

REFERENCE EXAMPLES 21 to 23

These Reference Examples were carried out in accordance with the procedure as described in the Examples but using hexene-1 as a raw olefin in place of propylene in an amount of 2.5 mole/l of the reaction solvent and using benzene in place of toluene as a reaction solvent. The reaction conditions used in these Reference Examples and the results obtained are shown in Table 7 below.

TABLE 7

Reference Example No.	Total Pressure (kg/cm²G)	Reaction Temperature (°C)	Concentration of Triphenylphosphine (m mole/litre reaction solvent)	n/i Ratio
21	100	110	3	1.18
22	50	110	3	2.66
23	30	110	3	2.68

Having regard to the provisions of Section 9 of the Patents Act, attention is directed to the claims of Patent No. 1,228,201.

WHAT WE CLAIM IS:—

1. A process for producing butyraldehydes which comprises reacting propylene with a water gas in a reaction solvent containing a triarylphosphine and a soluble rhodium complex in which a portion of said triarylphosphine is coordinated with rhodium metal, under a carbon monoxide-hydrogen total pressure of from 30 to 100 kg/cm² and at a temperature of from 60 to 150°C, the total amount of the triarylphosphine present in said reaction solvent and in said soluble rhodium complex coordinated with rhodium metal being from 1 to 30 m moles per litre of said reaction solvent.

2. A process according to Claim 1, wherein said soluble rhodium complex is present at a concentration of from 0.1 to 500 mg. calculated as rhodium metal, per litre of said reaction solvent.

3. A process according to Claim 2, wherein said soluble rhodium complex is present at a concentration of from 5 to 100 mg. calculated as rhodium metal, per litre of said reaction solvent.

4. A process according to any preceding Claim, wherein the ratio of said triarylphosphine and rhodium metal forming said soluble rhodium complex in said reaction solvent is from 5 to 200 moles of said triarylphosphine per gram-atom of said rhodium metal.

5. A process according to any preceding Claim, wherein said triarylphosphine is triphenylphosphine.

6. A process according to any preceding Claim, wherein the water gas consists of hydrogen and carbon monoxide in a proportion of ¹/₂ to 7 moles of hydrogen per mole of carbon monoxide.

7. A process for producing butyraldehydes which comprises continuously introducing (1) a reaction solvent containing a triaryl phosphine and a soluble rhodium complex in which a portion of said triaryl-phosphine is coordinated with rhodium metal, (2) propylene, (3) carbon monoxide and (4) hydrogen into a reaction zone maintained at a temperature of from 60 to 150°C and at a carbon monoxide-hydrogen total pressure of from 30 to 100 kg/cm³, distilling the resultant reaction mixture discharging from said reaction zone to isolate butyraldehydes as a distillate and recycling the remaining distillation residue comprising the soluble rhodium complex and the triarylphosphine to said reaction zone, the total amount of said triarylphosphine present in said reaction solvent and in said rhodium coordinated with rhodium metal being from 1 to 30 m moles per litre of said reaction solvent.

8. A process according to Claim 7, wherein the carbon monoxide (3) and the hydrogen (4) are introduced in a proportion of ¹/₂ to 7 moles of hydrogen per mole of said carbon monoxide.

9. A process according to Claim 7 or 8, wherein said soluble rhodium complex is present at a concentration of from 5 to 100 mg. calculated as rhodium metal, per litre of said reaction solvent.

10. A process according to Claim 1 or Claim 7 and substantially as hereinbefore described.

11. A process for producing butyraldehydes substantially as hereinbefore described with reference to any one of Examples 1 to 7.

12. A butyraldehyde when produced by a process as claimed in any preceding Claim.

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HYDROFORMYLATION REACTION OF PROPYLENE AT A TEMPERATURE OF 120°C.